Indian J. Phys. **78(8)**, 757-761 (2004)

AN INTERNATIONAL JOURNAL
IJP

Simple equilibrium statistical mechanical theory of hard non-sphere fluid mixtures

B P Karki and S K Sinha*

Department of Physics, L S College, B B A Bihar University, Muzaffarpur-842 001, Bihar, India

E-mail : sk_sinha_phy@yahoo.co.in

Abstract : Using the physical interpretation of the reciprocal of activity, an expression is derived for the equation of state of hard convex body fluid mixtures. The theory is applied to calculate the equation of state of the fluid mixture of hard dumbbells and fluid mixtures of hard spheres and prolate spherocylinder with $\gamma = 2$. In all these cases, the agreement with the simulation data is fairly good.

Keywords : Hard-convex body fluid mixture, reciprocal of activity, equation of state.

PACS Nos. : 05.70.Ce, 64.30.+t

1. Introduction

The present paper is concerned with the evaluation of equation of state of a fluid mixture of hard non-spherical molecules. This is because the hard non-sphere fluid mixture is as important in framing a theory of real molecular fluid mixture as the hard non-sphere fluid is in case of one-component molecular fluid. The simplest hard non-sphere fluid mixtures are the hard convex-body (HCB) fluid mixtures, such as hard ellipsoid of revolution (HER) fluid mixtures, hard dumbell (HDB) fluid mixtures and mixtures of hard spheres (HS) and hard spherocylinders (HSC). They have been extensively studied [1], because they can be model the shape of real molecules.

One of the theoretical approach is based on a physical interpretation of the reciprocal of activity. This approach has been employed by Andrews [2] for the hard sphere fluid and Andrews and Ellerby [3] for the hard sphere mixture. Recently this approach has been extended to the HCB fluid [4].

In the present paper, we extend this approach to derive the equation of state of the HCB fluid mixtures.

2. Basic theory

The chemical potential μ_i of the species i can be obtained from the partition function Q_N as

$$\mu_i = -kT \ln [Q_{N+1}/Q_N], \tag{1}$$

where the partition function Q_N for a linear molecular fluid mixture is given by

$$Q_N = \prod N_a! \lambda_a^{3N_a} q_a^{-N_a} \int \exp[-\beta U_N] \prod_{k=1}^{N} dx_k , \tag{2}$$

where

$$dx_k = (4\pi)^{-1} \, dr_k \, d\omega_k \tag{3}$$

and

$$U_N = \sum_{a,b} \sum_{k<l} u_{a,b}(x_k, x_l) . \tag{4}$$

$u_{ab}(x_k x_l)$ is the pair potential between molecule k of species a and molecule l of species b. Here $x_k = (r_k \omega_k)$ is the vector describing the position r_k of the center of mass and orientation ω_k of molecule k, $\beta = (kT)^{-1}$ (where k is the Boltzmann constant and T the absolute temperature) and N_a is the number of molecules of species a, such that the total number of molecules is

*Corresponding Author
Address for correspondence : Ramani Mohan Garden, Kalambag Road Chowk, Muzaffarpur-842 002, Bihar, India

$N = \sum_a N_a$. Further in eq. (2), λ_a is the thermal wavelength and q_a is the single-molecule rotational partition function of species a.

Substituting eq. (2) in eq. (1), we get

$$\mu_i(\rho,T,X) = \mu_i^0 - kT \ln a_i^{-1}(\rho,T,X), \tag{5}$$

where

$$\mu_i^0(\rho,T,X) = -kT \ln\left(V\lambda_i^{-3} q_i / N_i\right) = -kT \ln\left(\lambda_i^{-3} q_i / \rho_i\right) \tag{6}$$

$$Va_i^{-1}(\rho,T,X) = \int \exp[-\beta U_{N+1}] \prod_{k=1}^{N+1} dx_k$$

$$\Big/ \int \exp[-\beta U_N] \prod_{k=1}^{N} dx_k \tag{7}$$

Here, μ_i^0 is the chemical potential of species i in an ideal gas of density $\rho_i = \rho x_i$ and temperature T (where $\rho = N/V$ is the density and $x_i = N_i/N$ is the concentration of species i); and a_i is the activity of the species i, relative to that of the ideal gas at the same density and temperature. Eq. (7) can be simplified to give [4]

$$Va_i^{-1} = \int dx_{N+1} \exp[-2\beta U_{N+1,i}], \tag{8}$$

where

$$U_{N+1,i} = (1/2) \sum_{j=1}^{s} \sum_{k=1}^{N_j} u_{ij}(x_k, x_{N+1}) \tag{9}$$

is the potential energy of the $(N+1)$-th molecule of species i within the fluid mixture.

In order to perform the integration of eq. (8) the N molecules are fixed in a most likely configuration, then the $(N+1)$-th molecule of species i wanders throughout the whole system.

In terms of a_i^{-1}, the pressure of the molecular fluid mixture is given by [3]

$$P/\rho kT = \sum_{i=1}^{s} x_i \left[1 - \ln a_i^{-1} + (1/\rho) \int^{\rho} \ln a_i^{-1}(\rho', T, x) d\rho'\right] \tag{10}$$

3. Hard non-sphere fluid mixtures

We consider a fluid mixture of hard ellipsoid of revolution (HER) molecules having the major and minor axes $(2a_j)$ and $(2b_j)$, respectively. We calculate a_i^{-1} for the HER fluid mixture generalising the theory for the HER fluid [4] and hard spehere (HS) mixture [3]. a_i^{-1} is simply the probability that at a point $x = (r\omega)$ chosen at random the $(N+1)$-th molecule of species could be inserted. This probability is a measure as a product of two terms. The first term P_1 is the unconditional probability that the random chosen point x does not overlap one of the N molecules within V *i.e.*

$$P_i = V - \sum N_j (\pi/6)(2a_j)(2b_j)^2$$

$$= 1 - (\pi/6)\rho \sum_j x_j K_j \sigma_{jj}^3$$

$$= 1 - \rho \sum x_j L_j, \tag{11}$$

where

$$L_j = (\pi/6) K_j \sigma_j^3,$$

$$K_j = 2a_j/2b_j, \tag{12}$$

and $\sigma_{jj} = 2b_j$ is the width of a molecule of species j.

The second term is the conditional probability that no molecule will lie in additional volume in which the $(N+1)$-th molecule of species i is to be accommodated That additional volume is

$$S_{ij} = (\pi/6)(2a_i + 2a_j)(2b_i + 2b_j)^2 - (\pi/6)(2a_j)(2b_j)^2$$

$$= (\pi/6)\left[(K_i\sigma_{ii} + K_j\sigma_{jj})(\sigma_{ii} + \sigma_{jj})^2 - K_j \sigma_j^3\right]. \tag{13}$$

Then the conditional probability P_2 that all N molecules be outside the additional volume $\sum S_{jj}$ is given by

$$P_2 = 1 - \sum S_{ij}/(V - N\omega_i)$$

$$= \exp\left[-\rho \sum x_j S_{ij}/(1 - \rho\omega_i)\right] \tag{14}$$

where ω_i is an average volume effectively excluded to a molecule of species i by each molecule on the mixture, when they are closed packed and $V - N\omega_i$ is the free volume. Thus, a_i^{-1} is given by

$$a_i^{-1} = P_1 P_2 = 1 - \rho \sum x_j Lj \,|\exp| - \rho \sum x_j S_{ij} / (1 - \rho \omega_i) \tag{15}$$

The quantity ω_i can be computed following the method of Andrews and Ellerby [2,3]. Thus,

$$\omega_i = \omega_i^L + (\rho / \rho_0)\left(\omega_i^H - \omega_i^L\right), \tag{16}$$

where ω_i^L and ω_i^H are low and high density values of ω_i, respectively, and ρ_0 is the closed packed density. For the HER fluid mixutre, $\rho_0 = \sqrt{2} / \sum_j x_j K_j \sigma_{jj}^3$ We can write $\omega_i^L = \sum_j x_j \omega_{ij}^L$ and $\omega_i^H = \sum_j x_j \omega_{ij}^H$, where ω_{ij} is the average volume effectively excluded to a HER of species i by HER of species J in the fluid mixture. Following the method of Andrews and Ellerby [3], it can be shown that

$$\omega_{ij}^L = M_{JJ} B_2^{jj} \delta_{ij}, \tag{17}$$

where

$$M_{jj} = \left[48\left(B_3^{jj} / B_2^{jj^2}\right) - 1\right] / 56, \tag{18a}$$

$$\delta_{ij} = (1/4M_{ij}) + \left(1 - (1/4M_{ij})\right)\left(K_i^{1/3}\sigma_{ii} / K_j^{1/3}\sigma_{jj}\right)$$

$$\text{for } \left(K_i^{1/3}\sigma_{ii} / K_j^{1/3}\sigma_{jj}\right) < 1$$

$$= 1 \text{ for } \left(K_i^{1/3}\sigma_{ii} / K_j^{1/3}\sigma_{jj}\right) > 1. \tag{18b}$$

Here B_2^{jj} and B_3^{jj} are, respectively, the second and third virial coefficient of the HER fluid of species j. In the high density limit, ω_i^H is given by

$$\omega_i^H = \rho_0^{-1} = \sum x_j K_j \sigma_{jj}^3 / \sqrt{2}. \tag{19}$$

Finally, we obtain a simple expression for a_i^{-1} for the HER fluid mixture

$$a_i^{-1} = (1 - Cz)\, \exp[-A_i z/(1 - \beta_i z + \gamma_i z^2)], \tag{20}$$

where

$$z = \rho / \rho_0 = \rho \sum x_j K_j \sigma_{jj}^3 / \sqrt{2} = \eta / (\pi \sqrt{2/6}), \tag{21a}$$

$$C = \rho_0 \sum_j x_i L_j = \pi\sqrt{2}/6 = 0.74048, \tag{21b}$$

$$A_i = \rho_0 \sum_j x_j S_{ij}, \tag{21c}$$

$$\beta_i = 1 + \gamma_i = \rho_0 \omega_i^L = \rho_0 \sum_j x_j \omega_{ij}^L. \tag{21d}$$

Here, the packing fraction η is defined as

$$\eta = (\pi/6)\rho \sum_j x_j K_j \rho_{jj}^3. \tag{22}$$

Substituting eq. (20) in eq. (10), we obtain an expression for pressure of the HER fluid mixture

$$P/\rho kT = \sum_i x_i \Big[\left(A_i z/(1 - \beta_i z + \gamma_i z^2\right) - (1/Cz)\ln(1 - Cz)$$

$$- \left(A_i / 2\gamma_i z\right)\ln\left(1 - \beta_i z + \gamma_i z^2\right)$$

$$- \left(A_i \beta_i / 2\gamma_i (1 - \gamma_i)\right)\ln\left(1 - \gamma_i z)/(1 - z)\right) \Big]. \tag{23}$$

The functional form of eq. (23) is similar to that found for the hard sphere (HS) mixture. By putting $K_j = 1$ it reduces the corresponding result for the HS mixture.

The coefficients β_i and γ_i of eq. (23) are expressed in terms of B_2^{jj} and B_3^{jj}. For the HER fluid of species j, they are given by [1]

$$B_3^{jj} = (1 + 3\alpha_j) V_m^j \tag{24a}$$

and

$$B_3^{jj} = (1 + 6\alpha_j + 6\alpha_j^2) V_m^j, \tag{24b}$$

$$V_m^i = (\pi/6) K_j \sigma_{jj}^3$$

is the volume of a HER molecule of species j and α_j is the shape factor defined by

$$\alpha_j = R_j S_j / 3V_m^i \tag{25}$$

Here R_j is the $(1/4\pi)$ multiple of the mean curvature integral and S_j the mean surface area.

4. Binary mixtures

For binary mixture with species 1 and 2, the packing fraction η is defined as

$$\eta = (\pi/6)\rho\left[x_1 K_1 \sigma_{11}^3 + x_2 k_2 \sigma_{22}^3\right]. \quad (26)$$

Thus, the coefficients (eqs. 21) reduce to

$$A_1 = C\left(7x_1K_1 + x_2\left[(K_1 + K_2R)(1+R)^2 - k_2R^3\right]\right)/$$

$$(x_1K_1 + x_2K_2R^3), \quad (27)$$

$$A_2 = C\left(x_1\left[(K_1 + K_2R)(1+R)^2 - K_1\right] + 7x_2K_2R^3\right)/$$

$$(x_1K_1 + x_2K_2R^3), \quad (28)$$

$$\beta_1 = 1+\gamma_1 = C\left[x_1K_1M_{11}(1+3\alpha_1)\delta_{11} + x_2K_2M_{22}(1+3\alpha_2)\right.$$

$$\left.\delta_{12}R^3\right]/(x_1K_1 + x_2K_2R^3), \quad (29)$$

$$\beta_2 = 1+\gamma_2 = C\left[x_1K_1M_{11}(1+3\alpha_1)\delta_{21} + x_2K_2M_{22}(1+3\alpha_2)\right.$$

$$\left.\delta_{22}R^3\right]/(x_1K_1 + x_2K_2R^3), \quad (30)$$

where $R = \sigma_{22}/\sigma_{11}$, $\delta_{11} = \delta_{22} = 1$ and δ_{12} and δ_{21} are obtained from eq.(18).

We apply the proposed theory to calculate the equation of state of the binary mixtures of hard non-spherical molecules.

We first calculate the coefficients A_i and β_i for the binary mixtures with $x_1 = x_2 = 0.5$ for the following two conditions

(i) When $\sigma_{11} = \sigma_{22}$, $R = 1$, we have

$$A_1 = C(11K_1 + 3K_2)/(K_1 + K_2), \quad (31a)$$

$$A_2 = C(3K_1 + 11K_2)/(K_1 + K_2), \quad (31b)$$

$$\beta_1 = 1 + \gamma_1 = C[M_{11}(1+3\alpha_1)K_1 + M_{22}(1+3\alpha_2)K_2$$

$$\delta_{12}]/(K_1 + K_2), \quad (32a)$$

$$\beta_2 = 1 + \gamma_2 = C[M_{11}(1+3\alpha_1)K_1\delta_{21} + M_{22}(1+3\alpha_2)K_2]$$

$$/(K_1 + K_2) \quad (32b)$$

and

(ii) When $\nu_1 = \nu_2$, $R \neq 1$, we have

$$A_1 = C(7K_1 + [(K_1 + K_2R)(1+R)^2 - K_2R^3])$$

$$/(K_1 + K_2R^3), \quad (33a)$$

$$A_2 = C([(K_1 + K_2R)(1 + R)^2 - K_1] + 7K_2R^3)$$

$$/(K_1 + K_2R^3), \quad (33b)$$

$$\beta_1 = 1 + \gamma_1 = C[M_{11}(1+3\alpha_1)K_1 + M_{22}(1+3\alpha_2)K_2R^3$$

$$\delta_{12}]/(K_1 + K_2R^3), \quad (34a)$$

$$\beta_2 = 1 + \gamma_2 = C[M_{11}(1+3\alpha_1)K_1\delta_{21} +$$

$$M_{22}(1+3\alpha_2)K_2R^3]/(K_1 + K_2R^3). \quad (34b)$$

4.1. Mixtures of hard dumbells :

We consider the binary mixtures of hard dumbell (HDB) with the site-site elongation $L_j^* = L_i/\sigma_{ii}$. We first define the corresponding HER for a given HDB, such that $\sigma_i^{HER} = \sigma_i^H$ and $V_i^{HER} = V_i^{HDB}$ *i.e.*

$$(\pi/6)K_i\sigma_i^{HER3} = (\pi/6)\sigma_i^{HDB}[1 + 3L_i^*/2 - L_i^{*3}/2]$$

or

$$K_i = 1 + 3L_i^*/2 - L_i^{*3}/2 \quad (35a)$$

In this cases, we have [1]

$$\alpha_i = (1 + L_i^*)(2 + L_i^*)/(2 + 3L_i^* - L_i^{*3}) \quad (35b)$$

We obtain K_i and α_i for a given value of L_i^*. Then values of A_i, β_i and γ_i are calculated for the equimolar (*i.e.* $x_1 = x_2 = 0.5$) mixtures. The values of A_i and β_i for equimolar HDB mixtures under conditions (i) $\sigma_{11} = \sigma_{22}$ and (ii) $\nu_1 = \nu_2$ as reported in Table 1 for different values of L_1^* and L_2^*. They depend on the condition as well as the values of L_1^* and L_2^*. When $\nu_1 = \nu_2$ we find that $A_1 = A_2$ and $\beta_1 = \beta_2$. We employ eq. (23) to calculate the equation of state, $P/\rho kT$ of equimolar HDB fluid mixtures under the conditions (i) $\sigma_{11} = \sigma_{22}$ and (ii) $\nu_1 = \nu_2$. The calculated results are compared with the 'exact' simulation data [1] in Tables 2 and 3 for different values of L_1^* and L_2^* at different η. The agreement is good particularly for

Table 1. Values of A_i and β_i of equimolar mixtures of hard dumbells.

L_1^*/L_2^*	A_1	A_2	β_1	β_2
		$\sigma_{11} = \sigma_{22}$		
0.6/0.0	6.02356	4.34316	1.60253	1.40522
1.0/0.0	6.17067	4.19605	1.75143	1.58701
0.4/0.2	5.46466	4.90206	1.56571	1.53870
0.6/0.2	5.65911	4.70761	1.60430	1.55601
		$\nu_1 = \nu_2$		
0.6/0.0	5.26815	5.26815	1.58736	1.58736
1.0/0.0	5.30354	5.30354	1.69703	1.69703
0.6/0.3	5.19544	5.19545	1.60104	1.60104
1.0/0.6	5.18634	5.18634	1.75054	1.75054

Table 2. Equation of state $P/\rho kT$ of equimolar mixtures of hard dumbells with $\sigma_{11} = \sigma_{22}$.

L_1^*/L_2^*		Theory	Exact
0.4/0.2	0.0750	1.37	1.41
	0.1500	1.91	2.02
	0.2249	2.72	2.94
	0.2999	4.00	4.58
	0.3749	6.08	7.54
0.6/0.2	0.0808	1.40	1.47
	0.1617	2.02	2.22
	0.2425	3.00	3.39
	0.3234	4.61	5.50
	0.4042	7.41	9.34
0.6/0.0	0.30	3.95	4.20
	0.45	9.49	10.15
1.0/0.0	0.30	4.26	4.88
	0.43	9.64	11.06

Table 3. Equation of state $P/\rho kT$ of equimolar mixtures of hard dumbells with $v_{11} = v_{22}$.

L_1^*/L_2^*		Theory	Exact
0.6/0.0	0.30	4.11	4.25
	0.45	10.15	10.27
1.0/0.0	0.30	4.35	4.83
	0.45	9.88	10.71
0.6/0.3	0.30	4.09	4.30
	0.45	10.16	10.52
1.0/0.6	0.45	11.84	13.27

low value of η and/or low values of L_1^*/L_2^*.

4.2. Mixtures of hard spheres and prolate spherocylinders :

Next we apply the theory to calculate the equation of state of binary mixtures of (1) hard spheres (HS) and (2) prolate spherocylinders (PSC). For this case, we assume that $\sigma_{ii}^{HER} = \sigma_{ii}^{PSC}$ and $v_i^{HER} = v_i^{PSC}$ *i.e.*

$$(\pi/6)K_i\sigma_{ii}^{HER^3} = (\pi/12)(3\gamma_i - 1)\sigma_{ii}^{PSC^3}$$

Table 4. Equation of state $P/\rho kT$ of equimolar mixtures of (1) hard spheres and (2) prolate spherocylinders of $\gamma = 2$.

Conditions		Theory	Exact
	0.20	2.42	2.50
	0.30	4.04	4.10
	0.40	7.18	7.31
	0.45	9.91	9.87
	0.20	2.49	2.52
	0.30	4.20	4.20
	0.40	7.55	7.39
	0.45	10.49	10.22

or

$$K_i = (3\gamma_i - 1)/2,$$

where γ_i is the ratio of maximum length $\left(L_i + \sigma_{ii}^{PSC}\right)$ and width σ_{ii}^{PSC}. The shape parameter α_i is given by

$$\alpha_i = \gamma_i(\gamma_i + 1)/(3\gamma_i - 1) \text{ for PSC,}$$
$$= 1 \qquad \text{for HS.} \qquad (37)$$

We calculate K and α for $\gamma = 2$ and other coefficients appearing in eqs. (31)–(34) for $x_1 = x_2 = 0.5$. The equation of state, $P/\rho kT$ of the equimolar mixtures of HS and PSC with $\gamma = 2$ are compared with the 'exact' results [1] in Table 4 for different values of η under (i) $\sigma_{HS} = \sigma_{PSC}$ and (ii) $v_{HS} = v_{PSC}$. The agreement is excellent.

5. Concluding remarks

Probability arguments employed by Andrews and Ellerby [3] for hard sphere are extended here to give simple expression for the equation of state for the HCB fluid mixtures. The theory is employed calculate the results for the HDB fluid mixtures and mixture of HS and PSC. The agreement is good when compared with the simulation data.

References

[1] T Boublick and I Nezbeda *Colln. Czech. Chem. Commun.* **51** 2301 (1986)

[2] F C Andrews *J. Chem. Phys.* **62** 272 (1975); **64** 1941 (1976)

[3] F C Andrews and H M Ellerby *J. Chem. Phys.* **75** 3542 (1981)

[4] T K Dey, S S Karki and S K Sinha *Indian J. Phys.* **78** 751 (2004)